

The University of Chicago

I. ASYMMETRIC ADSORPTION ON
DEXTRO QUARTZ

II. THE TSWETT COLUMN, AN EXPERIMENTAL
STUDY

III. PHOTOELECTRIC POLARIMETRY
A THEORETICAL STUDY

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

By

AARON MAYER ALTSCHUL

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PREFACE

The first phase of the problem was to determine asymmetric adsorption on a quartz column. This work led to results which were not clearly defined because the detecting instruments were not sensitive enough. As a result, the construction of a sensitive polariscope was undertaken. Since the original work was done with a Tswett column, a systematic study of this column was also made.

This dissertation is, therefore, composed of three parts:

- I. Asymmetric adsorption on dextro quartz.
- II. The Tswett column, an experimental study.
- III. Photoelectric polarimetry, a theoretical study.

The author is pleased to acknowledge his indebtedness to Dr. Thorfin R. Hogness for timely aid and advice, and constant encouragement during the course of the research.

The author also wishes to thank Dr. Simon Freed and Dr. Albert E. Sidwell, Jr. for kindly discussion and assistance in certain portions of the work.

The author wishes to express his appreciation to his colleague, Mr. Fred Karush, and to Mr. Raymond Mesirow, Mr. Franklin Offner, and Mr. Sam Weissman for valuable assistance in the work on the polariscope.

I. ASYMMETRIC ADSORPTION ON DEXTRO QUARTZ

Most biological reactions involving optically active substances proceed in unsymmetrical fashion producing only one of the optical antipodes. Many attempts have been made to duplicate such reactions in the laboratory when optically active reagents are allowed to react in asymmetric media. Fajans¹ reported that a racemic mixture of camphoric acid upon decarboxylation in optically active nicotine solution gives optical rotation as high as 1.5° . In another experiment,² cinnamic acid and levulose were put into a water solution, heated for a while, and then evaporated to dryness. When bromine was added to this mixture, the di-brom compound showed optical activity. Optically active quartz covered with Ni was used to catalyze the dehydration of secondary butyl alcohol to give optically active products as reported by Schwab.³ When this experiment was repeated by Tsuchida,⁴ no optical activity was found.

Attempts have been made to deracemize optically inactive mixtures by adsorption on optically active adsorbents. Peter⁵ reported optical activity when a racemic dye was treated with wool. This result could not be repeated by Brode.⁶ Asymmetric

¹Fajans, Z. physiol. Chem., 73, 36 (1910).

²Erlenmeyer, Biochem. Z., 133, 57 (1922).

³Schwab, Post, and Rudolph, Kolloid-Z., 68, 157 (1934).

⁴Tsuchida, Kobayashi and Nakamura, Bull. Chem. Soc. Japan, II, 38 (1936).

⁵Peter and Ihrig, J. Am. Chem. Soc., 45, 1992 (1923).

⁶Brode and Adams, ibid., 48, 2202 (1926).

adsorption on nerve tissue was reported by Richter.¹ Using dextro and laevo quartz powders, Japanese workers observed deracemization with mixtures of complex inorganic salts.² In all cases of asymmetric adsorption, the optical activity reported was very small, of the order of 0.02° . Unless the error involved in reading the rotation is considerably less, these figures cannot be considered as reliable. Since the accuracy of the polarimeter used is not given in any of the reported works, the results must be accepted with some reserve.

The deracemization due to asymmetric adsorption is very small because there is very little selective adsorption between the two optically active antipodes. It was thought, however, that the use of a Tswett column (described in Part II) which multiplies small selective adsorption effects considerably, might conceivably give more easily measured results. Accordingly, a long glass tube (2 ft.) was packed with dextro quartz ground to 200 mesh. It was expected that the first portion which comes through the column should show the maximum deracemization and, therefore, the maximum rotation.

Using n-butyl lactate on a dextro quartz column, no deracemization was observed. When α brom propionic acid was used, the first portion showed a rotation of 0.14° . The error involved in making the reading was 0.04° . Inasmuch as small rotations must be read, it was recognized that a much more sensitive polarimeter must be used before reliable results could be reported. The investigation was, therefore, discontinued until a sensitive polarimeter could be obtained.

¹Richter and Dosser, Biochem. Z., 268, 400 (1934).

²Tsuchida, op. cit., p. 38. Kobayashi and Nakamura, J. Chem. Soc. Japan, 56, 1339 (1936).

II. THE TSWETT COLUMN, AN EXPERIMENTAL STUDY

Introduction

In 1906, M. Tswett, a botanist working on the isomers of chlorophyll, published a new method for the separation of isomers which differ very slightly in their physical properties.¹ He packed a tube with powdered sugar and filtered his leaf extract through it. The substances in the solution were adsorbed in differently colored layers, one below the other, while the solvent filtered through clear. It was then a simple matter to dig out the separate layers, wash off their pigments, and isolate the components of the extract. Although more than one treatment was necessary to purify each isomer completely, the method of separation employed was, for these particular types of substances, far superior to other physical processes. He called this procedure "Chromatographic Adsorption Analysis" and the column used was later called the Tswett column.

The value of Chromatographic Adsorption Analysis was not recognized until about twenty years later. Since then, however, its use has been widely extended and its applications cover many different fields. An excellent survey of the entire field of work done with the column and a complete up to date bibliography are given in a recent book by Zechmeister.²

¹M. Tswett, Ber. der deutschen botanischen Gesellschaft, 24, 384 (1906).

²L. Zechmeister and L. v. Cholnoky, "Die Chromatographische Adsorptionsmethode," Julius Springer, Vienna, 1937.

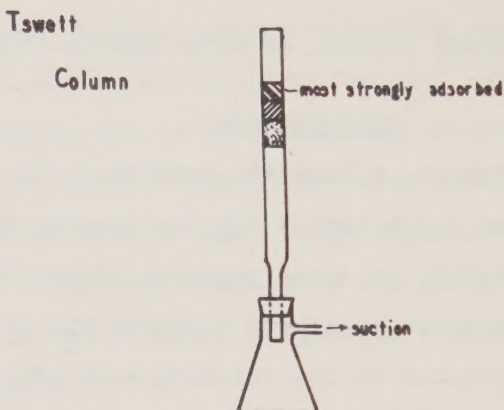


Fig. 1

The conditions necessary for a good separation are better understood if an abstract problem is considered. Pure A and B must be recovered from a solution containing a mixture of these two substances. The first step is to find a powdered adsorbent which will selectively adsorb one of these two components from the solution. When the solution of A and B is passed over a column packed with this adsorbent, two contiguous layers are formed. One layer will contain a high percentage of A and the other will have a high percentage of B. To complete the separation, the column is washed with more solvent until the layers are distinctly separated. If, however, A and B are too strongly adsorbed on the column, it will be impossible to accomplish separation by washing the column with more solvent.

Having achieved the desired separation, pure A and B must be recovered from their respective sections on the column. Recovery is usually accomplished either by washing the powder with an excess of the original solvent or by elution with a liquid which has a greater affinity for the surface of the adsorbent

than the substance adsorbed and, therefore, displaces the latter from the powder.

Neither A or B must undergo chemical change during the process of separation by reaction with the adsorbent.

As a result of the numerous separations made by use of the column, a number of empirical rules have been formulated to aid the investigator. As yet, however, no quantitative explanation of what happens on the column has been given.

The equilibrium expression for the selective adsorption in the hypothetical example given above may be represented by a modification of Langmuir's equation

$$\theta_A = \frac{MC_A}{1 + MC_A + NC_B},$$

$$\theta_B = \frac{NC_B}{1 + MC_A + NC_B}$$

in which:

θ is the fraction of the surface of the solid covered by the particular component,

C is the concentration of the components in the solution in equilibrium with the solid,

M and N are constants.

If the selective adsorption is very small, the composition of the solution in equilibrium with the solid will be but slightly changed from the original composition. Thus it would be impossible to separate A and B from a solution containing a mixture of both of them by merely shaking the solution with some of the solid adsorbent. If, however, the same solution were passed over a Tswett column packed with the same adsorbent, complete separation would be achieved.

It is apparent that the slight separation resulting from the selective adsorption on the adsorbent is magnified considerably

by the Tswett column. This magnification suggests that a kinetic action is involved and that the amount of separation is dependent on the rate of washing of the components on the adsorbent by the flowing solvent.

A complete discussion of the column is possible only when quantitative information as to what actually happens on the column is available. It was, therefore, found necessary to devise a method for studying the concentration gradient of the adsorbed substances down a column.

Experimental Method

The concentration gradient is defined as the rate of change of the concentration of the adsorbed material on the adsorbent from the top of the zone of adsorption on the column to the bottom.



Fig. 2

Let us divide the zone in Fig. 2 into n sections. Each section, i , has a concentration of adsorbed substance C_i , weight of adsorbent, W_i , and distance from top of the zone, X_i . By plotting C_i against X_i for i varying from 1 to n , a concentration gradient curve is obtained. A bar graph must be used because C_i represents an average concentration for the section i . To make this method of plotting independent of the diameter of the tube used, $\sum_{i=1}^n W_i$ is used instead of X_i .

Suppose, for example, the zone is divided into four sections. The concentration gradient curve would be obtained as shown in Fig. 3.

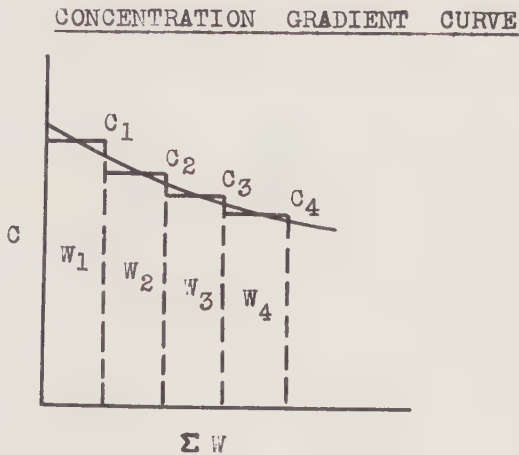


Fig. 3

In order to determine experimentally the concentration gradient, it is necessary to remove the packed column of adsorbent after it has been covered with the adsorbed material, slice it at regular intervals, remove the adsorbed substance, and determine the amount of substance adsorbed on each slice. A simple glass apparatus, shown in Fig. 4, may be used to hold the column of adsorbent. The top of the tube at which the slicing will take place is ground down so that there will be a plane surface upon which to slice. The bottom of the tube is plugged first with a little wad of glass wool, to prevent the adsorbent from going through into the suction flask, and then with a perforated cork stopper.

When the glass apparatus is set up as described, the adsorbent is suspended in the liquid to be used as a solvent and washed into the tube. With the aid of suction, the solid is



Fig. 4

drawn down into the tube and packed well. The top of the solid adsorbent is then packed firmly with a piston. This latter action insures a well packed column which does not break when pushed out of the tube. It is necessary that all the needed adsorbent suspension be added first and sucked dry before the top is packed down. This procedure prevents the formation of layers within the column and the resulting distortion of the concentration gradient.

When the packing is completed, a perforated porcelain disc is put on the top of the column to protect it when liquid is dropped down. Solvent is then added through a dropping funnel fitted in a cork and the suction adjusted until the liquid filters through at the rate of about one drop per second. Once the rate of flow is adjusted, the liquid is sucked through until a very thin layer remains above the top of the column. The solution containing the material to be adsorbed is then added. If the column is to be washed with more solvent after the adsorption has taken place, the fresh solvent is added just before the last part of the solution has disappeared from the top. Once the experiment is started and suction applied, the liquid above the column

should not be allowed to run dry until the entire solution is passed over the column. The method described, which is an adaptation of the method used by Winterstein,¹ gives fairly uniform packing and results in an even distribution of the adsorbed material throughout the cross section of the column.

When the column is sucked dry of all solvent, the tube is removed from the suction flask and fastened securely in a horizontal position. The column of adsorbent is pushed out gently and sliced. The slices are weighed, the adsorbed material eluted with a suitable solvent, and filtered into volumetric flasks.

When colored substances are separated by the column, analysis is easily made by a spectrophotometric method.²

Using α carotene as the adsorbed substance, the method of analysis was found to be 88% efficient (overall) in removing the adsorbed substance from the column. When tested with picric acid as the substance to be adsorbed, the maximum error in reproducibility was found to be $\pm 10\%$. At first glance, the amount of error would tend to indicate that this method is unreliable for determining accurate concentration gradient curves. When used as a statistical method, however, the curves obtained may be considered quite reliable.

The principal criticism of this method is that it is too tedious and indirect. Yet it is difficult to see how observations directly on the column without removing it from the glass tube could furnish the required information.

¹Winterstein and Schön, Zeitschrift physiol. Chem., 230, 139 (1934).

²Zscheile, Hogness, and Young, J. Phys. Chem., 38, 1 (1934). Hogness, Zscheile, and Sidwell, ibid., 41, 379 (1937).

Experimental Results

Series 1

The first substance tried by this method was α carotene obtained from the S. M. A. Corporation. A low boiling petroleum ether was used as the solvent while absolute ethyl alcohol was used as the eluting agent. The adsorbent was a 1:1 mixture of MgO and silicious earth.

Experiment 1

A sample of 9.5 mg. of carotene was dissolved in 250 cc. of petroleum ether. 25 cc. of this solution was put on a MgO column packed in a tube with an inside diameter of 24 mm. At the conclusion of the run, 15, 2 mm. slices with an average weight of 0.50 g. were taken off. The eluted solutions in absolute alcohol were put into 50 cc. volumetric flasks.

Assuming that Beer's law holds for α carotene solutions, it was possible to determine the concentration of the solutions spectroscopically.

$$\log I_0/I = \alpha c l$$

where I_0 is the light intensity through the pure solvent, I , the intensity of light coming through the cell containing the carotene solution, α , the specific absorption coefficient of α carotene, c , the concentration in grams/liter, and l , the length of the absorption cell. For $\lambda = 4460 \text{ \AA}$, $\alpha = 257.^1$ The concentration gradient curve is shown in Fig. 5.

Experiment 2

This experiment was like the preceding one except that 45 cc. of diluted, 1:1, α carotene solution were used. The

¹E. Miller, Botanical Gazette, 96, 447 (1935).

curve of the results shown in Fig. 5 is very similar to the one obtained in the previous experiment.

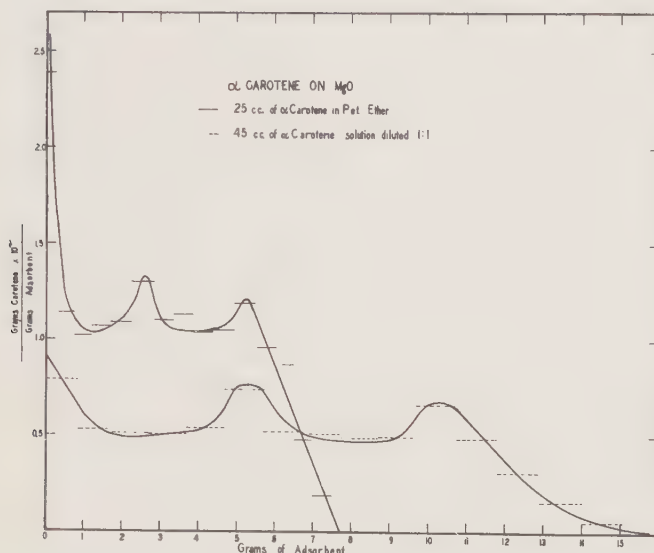


Fig. 5.--Experiments 1 and 2, Series 1

Experiment 3

The conditions were varied somewhat in this run. A sample of 25 cc. was run through a column prepared as above and washed with an additional 25 cc. of petroleum ether. In this case, the curve of the results, Fig. 6, is symmetrical. The two maxima appearing in the first two experiments are seen here too.

Experiment 4

The effect of change of adsorbent on the structure of the curve obtained was tested in the next two experiments. Powdered sugar (commercial sucrose) was packed in the columns and used as the adsorbent. Sucrose does not adsorb carotene strongly with the result that some of the carotene solution filtered through into the suction flask. A sample of 25 cc. of α carotene solution was run through the column. Seventeen slices of average

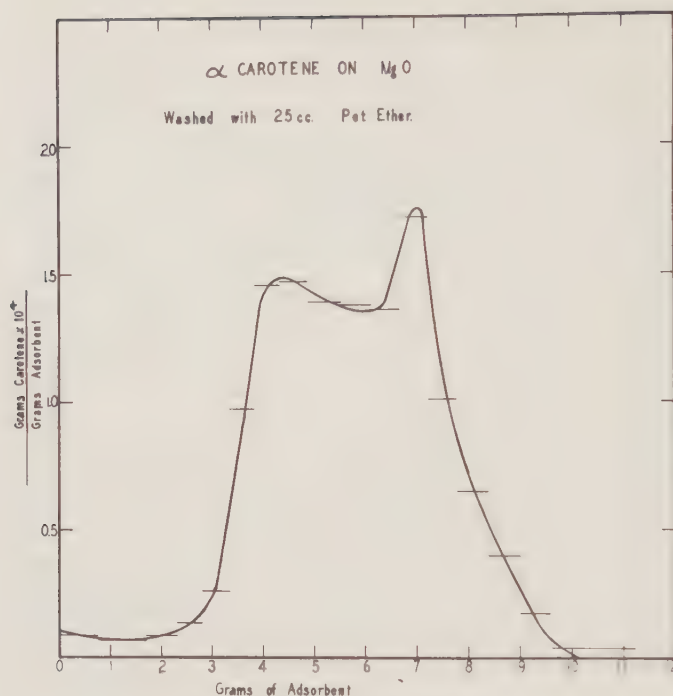


Fig. 6.--Experiment 3, Series 1

weight of 2.40 g. were analyzed. The curve of the results shown in Fig. 7 has well defined maxima.

Experiment 5

Experiment 4 was repeated. This time, however, smaller slices (average weight 1.75 g.) were taken. The resulting curve, Fig. 7, showed better separation of the maxima than the preceding one.

Before any attempt at explanation of the experimental results could be made, a second series of experiments with a different substance had to be made. Picric acid was selected because it is easily adsorbed from benzene solution by $CaCO_3$ and easily eluted from that surface by absolute alcohol. The picric acid was recrystallized from hot water, dried in a vacuum desiccator

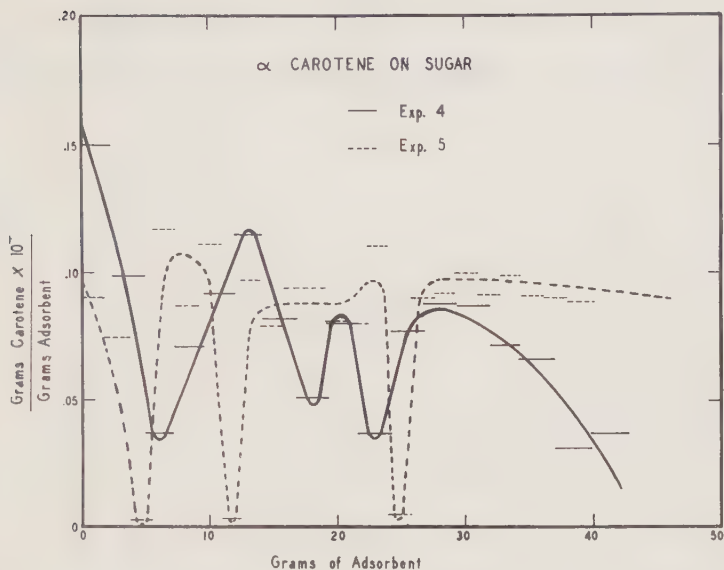


Fig. 7.--Experiments 4 and 5, Series 1

and dissolved in freshly distilled benzene. A 1:1 mixture of CaCO_3 and silicious earth was prepared for use as the adsorbent.

Series 2

Experiments 1 and 2

A sample of 20 cc. of picric acid solution was passed through a CaCO_3 column prepared as in the previous series.

Experiments 3 and 4

Here narrower tubes, 19 mm. in width, were used. The same procedure as in experiments 1 and 2 was followed. Just as in the case of α carotene, the concentration of the picric acid in the slices was determined spectroscopically.

The results of experiments 1, 2, 3, and 4 were plotted on one graph and the average values of the bars calculated. In order to decide how to plot this curve, the average error involved in this method was determined by packing a tube with CaCO_3 already

saturated with picric acid, slicing this column, and analyzing the slices. The maximum deviations from a straight line were determined as $\pm 10\%$. As a result, a smooth curve was drawn as shown in Fig. 8.

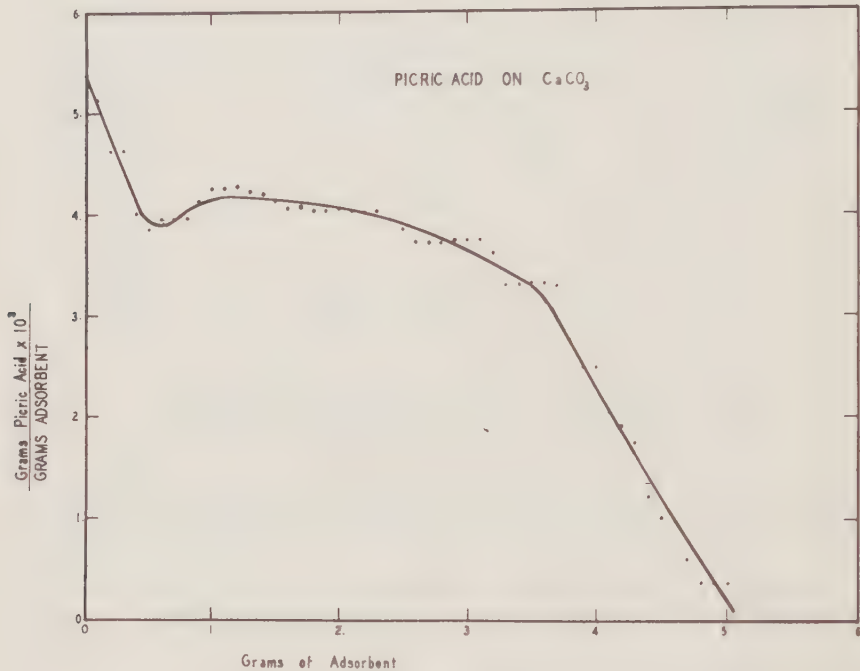


Fig. 8.--Experiments 1, 2, 3, and 4, Series 2

Discussion of Results

A. Theory of column

An experimental method has been developed to study the concentration gradient on a Tswett adsorption column. Using a pure substance like picric acid, it should be possible to study the form of the curves under various conditions of concentration and washing. By introducing a suitable second pure substance, the curves of both substances can be obtained and the effect of

one upon the other determined. When such experimental data are available, it will be possible to discuss the theory of the column quantitatively and determine what kinds of processes take place.

B. Behavior of α carotene

The concentration gradient curve of α carotene differs from that of picric acid in the fact that it shows two maxima. There were two possible explanations for this difference.

(1) Purified α carotene may actually consist of two or more stereoisomers having almost identical absorption spectra but having different affinities for an adsorbing surface. The absorption spectra of the solutions giving the peaks in Figs. 5 and 7 show no significant differences. Inasmuch as the spectrum analysis was the only available method for determining differences in structure, it was found impossible to check this hypothesis.

(2) The alternative explanation is that adsorption may take place periodically on the Tswett column. This latter hypothesis is suggested by the Liesegang ring and related phenomena which are found widespread in both natural and artificial media.¹ If, however, the latter explanation were correct, the amount of solution used should determine the number of maxima and minima in the concentration gradient curves. Curves of the results of experiments 1 and 2, Fig. 5, should accordingly exhibit a different number of maxima. The experiments show that for MgO only two maxima are observed. Thus it must be concluded that the maxima and minima observed are a result of a property of α carotene and not of the column.

¹Hedges and Myers, "The Problem of Physico-Chemical Periodicity," Longmans, Green and Co., New York, 1926.

New facts which have recently appeared in the literature have made it possible now to satisfactorily explain the α carotene curves. Gillam¹ reported that the upper and lower sections of an Al_2O_3 column upon which pure β carotene had been adsorbed gave two compounds with slightly different spectroscopic properties. One substance was β carotene, the other was called pseudo- α carotene. Similarly, when a large amount of α carotene was adsorbed on a MgO column, two substances, neo- α carotene and α carotene, were found. It can therefore be said with some degree of certainty that the two maxima of the curve of α carotene adsorbed on MgO indicate that two isomers are separated on the column.²

From the above considerations it is readily seen that the spectroscopic method of analysis is incapable in many instances of determining whether a substance is pure or contains isomers. Thus much of the current literature relating to substances described only by their absorption spectra is rendered ambiguous. The method of column analysis developed here may be used in a systematic investigation of the so called pure substances to determine whether any isomers can be found.

A Continuous Adsorption Column

The Tswett adsorption column in its present form cannot be used for large scale separations. When one column is saturated with adsorbed material, a new one is required for further work. It is possible, however, to design a column, based on the Tswett principle, which can be operated continuously.

¹Gillam and M. S. el Ridi, Biochem. Jour., 30, 1735 (1936).

²A further examination of α carotene on sugar may conceivably reveal more than two isomers.

CONTINUOUS ADSORPTION COLUMN

Model I

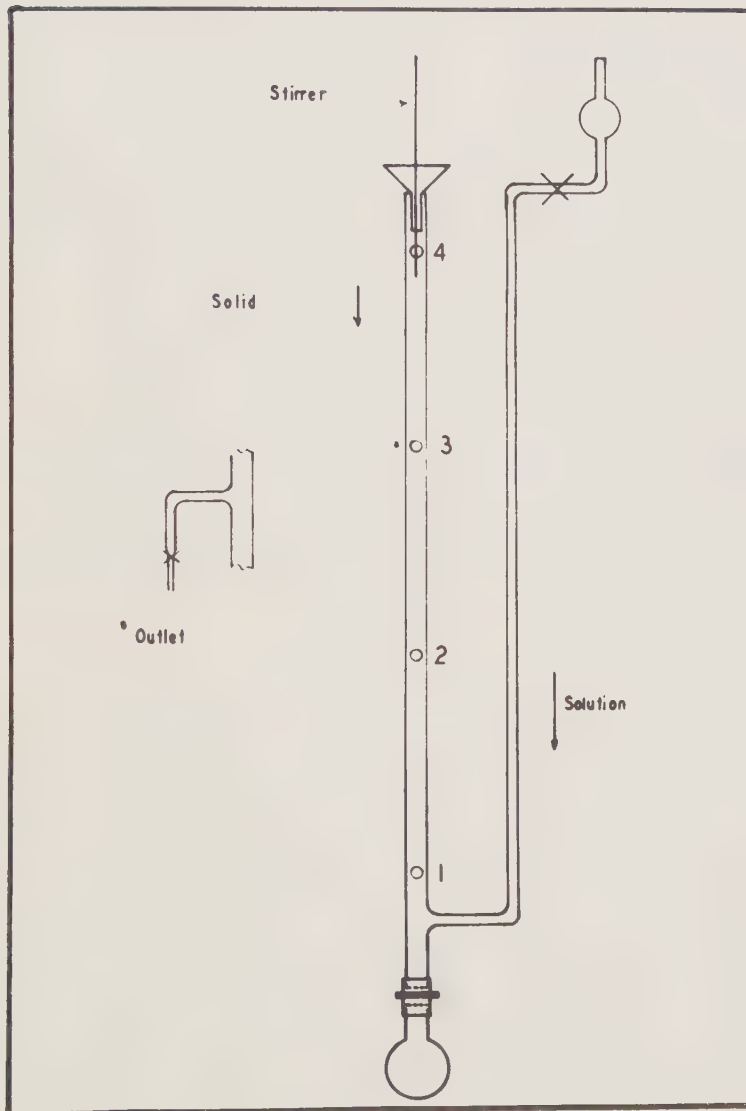


Fig. 9

The solution flows up a glass tube and comes out of an outlet on the top (Fig. 9). Solid adsorbent drops through this liquid and collects at the bottom in a flask from which it can be removed. If there is selective adsorption of the components in the solution, separation can be achieved by withdrawing the liquid from suitably placed outlets on the tube.

A laboratory model was constructed, as shown in Fig. 9, and tested. The solid adsorbent was dropped through a funnel at the top while the flow of solution caused by gravity was controlled by a stopcock. The total length of the column was about seven feet.

A solution of alizarin and picric acid dissolved in benzene was used to test this column. The absorption spectra of both alizarin and picric acid are shown in Fig. 10. For such

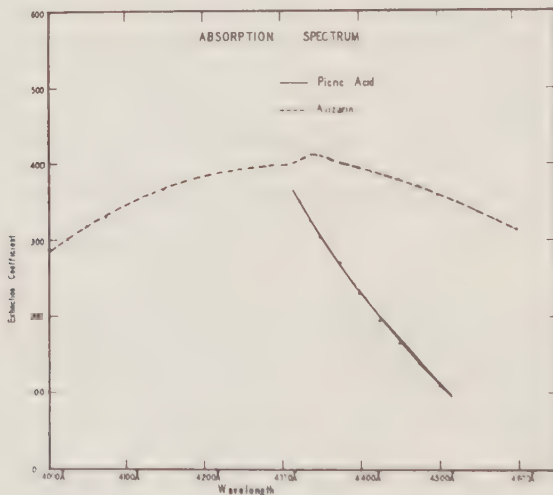


Fig. 10

a solution, the concentration of each component may be determined spectroscopically by solving simultaneous equations as follows:

Let

C_a = concentration of alizarin in g/liter,
 C_p = " " picric acid in g/liter,
 $\alpha_a^{\lambda_1}$ = absorption coefficient of alizarin for λ_1 ,
 $\alpha_a^{\lambda_2}$ = " " " " " λ_2 ,
 $\alpha_p^{\lambda_1}$ = " " " picric acid for λ_1 ,
 $\alpha_p^{\lambda_2}$ = " " " " " λ_2 ,
 l = length of absorption cell.

From Beer's law,

$$\alpha_a^{\lambda_1} C_a l + \alpha_p^{\lambda_1} C_p l = \log (I_0/I)_{\lambda_1},$$

$$\alpha_a^{\lambda_2} C_a l + \alpha_p^{\lambda_2} C_p l = \log (I_0/I)_{\lambda_2}.$$

If $\alpha_a^{\lambda_1}$, $\alpha_a^{\lambda_2}$, $\alpha_p^{\lambda_1}$, and $\alpha_p^{\lambda_2}$ are known, the value of C_a and C_p can be determined by getting $(I_0/I)_{\lambda_1}$ and $(I_0/I)_{\lambda_2}$.

The values of α used were:

	$\lambda = 4400 \text{ \AA}$	$\lambda = 4425 \text{ \AA}$
Alizarin	413	410
Picric Acid	245	207

During the test runs, solid suspension was withdrawn from different portions of the column. In order to get the alizarin into solution, it was necessary to destroy the adsorbent with acid. Since the adsorbent was CaCO_3 , this was a relatively easy matter. The substances were then dissolved in absolute alcohol and analyzed.

When the first solution containing both alizarin and picric acid was tried in the column, the following results were obtained.

	$\frac{C_a}{C_a + C_p} \times 100$	
Original solution	21	
Solution from #1 outlet . . .	43	
Solution from #3 outlet . . .	65	

The concentration of alizarin increased considerably when the liquid reached the top of the column. In order to be able to recover both substances in pure form, a change in design was made to allow the solution to enter the middle of the column as shown in Fig. 11. This time the results were:

	$\frac{C_a}{C_a + C_p} \times 100$	
Solution from #1 outlet . . .	1.1	
Original solution	3	
Solution from #4 outlet . .	19.3	

This model shows improvement in the fact that isolation of both components is taking place. On the other hand, very little separation is achieved below the point where the solution enters the main tube (Fig. 11). It therefore seems likely that model one (Fig. 9) built on a much larger scale will be able to give the desired results. By proper regulation of the rate of flow of the liquid, it should be possible to achieve the same degree of separation as obtained by an ordinary Tswett column.

It must be pointed out that care in the planning of the details of a continuous column, such as has here been shown to be theoretically possible, is necessary in order to have a practical column.

CONTINUOUS ADSORPTION COLUMN

Model 2

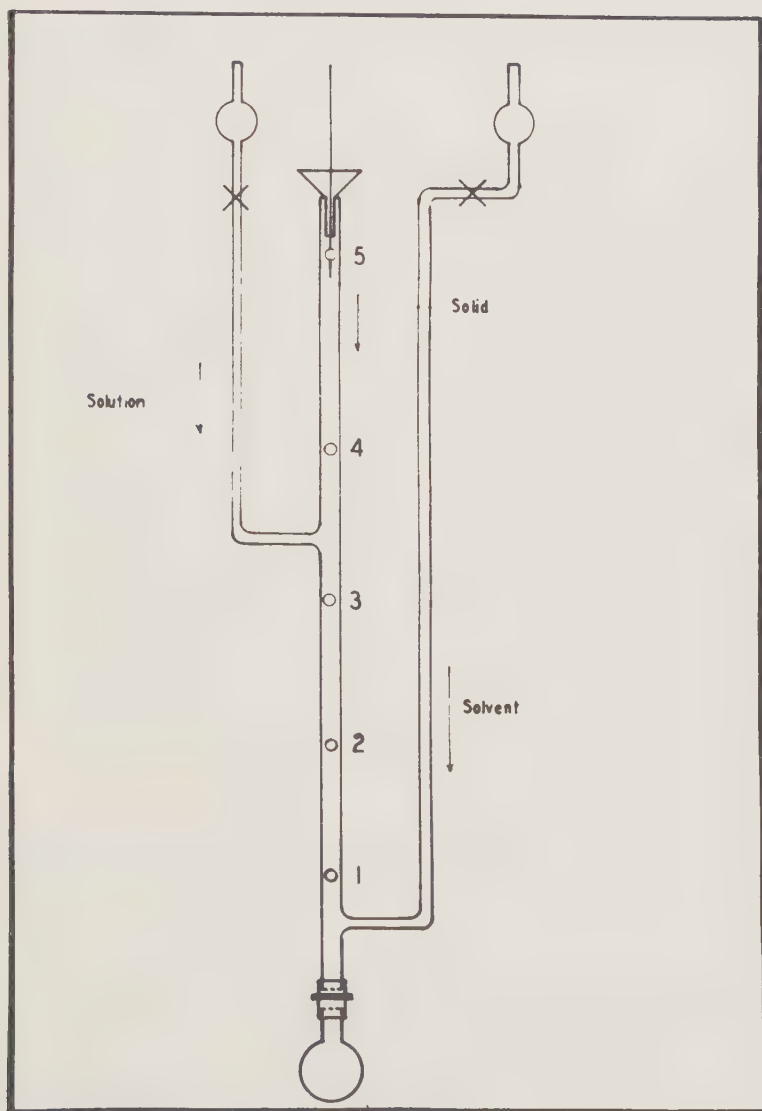


Fig. 11

III. PHOTOELECTRIC POLARIMETRY, A THEORETICAL STUDY

Introduction

In the course of an investigation on asymmetric adsorption on a quartz column, it was found necessary to construct a polariscope of high precision and sensitivity. A study of the principles involved in the existing types of polariscopes was made and a basis laid for the design of the instrument to be built.

The following represents a theoretical study of the polariscope. No attempt has been made to describe the details of the optical or electrical instruments involved because they have been adequately described elsewhere.¹

A review of the theory of the existing polariscopes has been made. This review, however, does not cover the entire field; only general types are taken as examples. Following the criticism of the polariscopes taken as examples, a theory of a new method is developed.

A description of the instrument itself will be postponed until it has been refined in all its details.

Comparison of Visual and Photoelectric Methods

(a) Visual methods

The simplest type of polariscope and historically the first to be used was the total extinction ocular polariscope.

¹T. M. Lowry, "Optical Rotatory Power," Longmans Green and Co., New York, 1935, Part II. "Handbuch der Physik," Julius Springer, Berlin, 1928, Vol. XVIII. G. Bruhat, "Traite de Polarimetrie," Revue d'optique theorique et instrumentale, Paris, 1930.



Total Extinction Polariscope

Fig. 12

P is a fixed polarizing prism which fixes the plane of polarization of the light passing through the optically active medium, O. To obtain the zero of the instrument, the analyzer, A, another polarizing crystal, is rotated until no light is seen by the observer, E. The rotation of the medium is the difference in the readings of the zero before and after the optically active medium is put in the optical path.

If θ is the angle between the planes of polarization of P and A, the intensity, I, of the light reaching the observer's eye is related to the original light intensity from the source, I_0 , by the following equation:¹

$$(1) \quad I = I_0 \cos^2 \theta.$$

If I is plotted as a function of θ , we can readily see the points where total extinction should be reported by an observer. Theoretically, total extinction should be reported only at the points where $\theta = (2n - 1) \pi/2$ (n is any integer). The eye, however, records total extinction before the theoretical extinction point is reached, as shown by the dotted line in Fig. 13. Thus there

¹In this and all following discussions, the optically active medium will not be considered a part of the optical path. This simplifies the calculations without in any way making any difference in the principles involved.

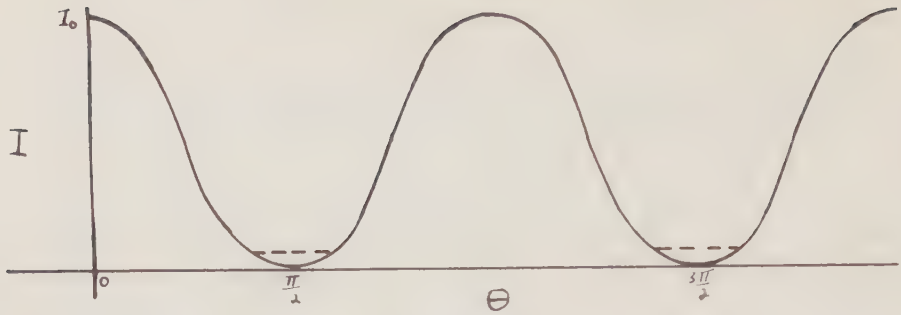
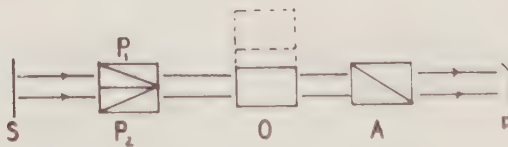


Fig. 13

is created an area of total extinction instead of a single point; with a corresponding increase in the error in determining the zero. This error is due to the fact that there is a threshold intensity below which the eye is not sensitive to light. For any single observer, the amount of eye fatigue at the moment of observation will influence the amount of error.

Another classical type of polariscope is the half-shadow instrument. The principle involved is the comparison of the intensity of two adjacent fields instead of the measurement of absolute intensity as used in the total extinction type. The split field is accomplished by two polarizing prisms or their



Half Shadow Polariscope

Fig. 14

equivalent placed in the position of the polarizer. There is a small angular difference, Δ , between the planes of polarization of the two prisms. The two equations for the intensity of the

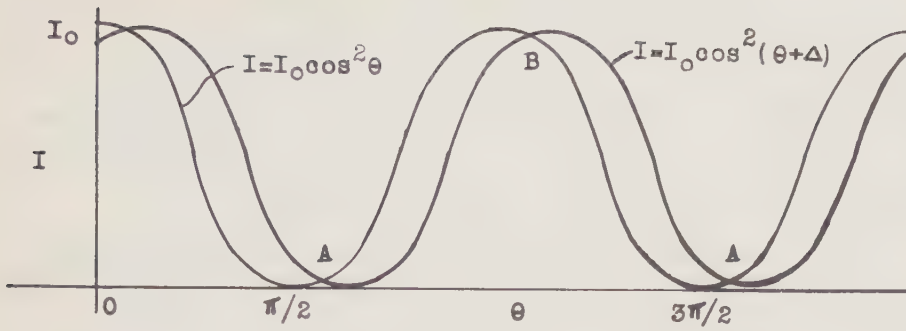


Fig. 15

light from the two fields are respectively:

$$(2a) \quad I_1 = I_0 \cos^2 \theta,$$

$$(2b) \quad I_2 = I_0 \cos^2 (\theta + \Delta).$$

For $\Delta \neq 0$, the intensities of the two fields will be equal when:

$$(3) \quad \theta = \tan^{-1} \frac{\cos \Delta - 1}{\sin \Delta}.$$

The values of θ determined by this equation represent the zeros of the instrument. Actually points of the type A, Fig. 15, instead of points B, are used. A study of the properties of the eye have resulted in the following empirical equation:¹

$$(4) \quad \Delta E = A \Delta H/H.$$

H is the total illumination of the field; A is a constant dependent on the eye of the observer; ΔH is the change in the illumination of the two half shadows; ΔE is the change in the sensitivity of the eye. Thus it can be seen that an increase in the total field intensity will result in a decrease in the sensitivity of the eye, hence the choice of points A, Fig. 15, instead of points B.

¹"Hand. der Physik," 1928, Vol. XVIII, p. 421.

The principal advantage of the half-shadow instrument over the total extinction apparatus is the fact that absolute light intensity is not measured thus obviating the error due to changes in intensity of the light source and removing the consideration of the sensitivity threshold of the eye.

Other attempts at ocular polariscopes have been made, and rather high sensitivities have been reported. Nevertheless, the ocular method, subject to the physiological limitations of the eye, cannot be the best method with which to record scientific facts. With the advent of the photo-electric cell, attempts were made to substitute this method of observation for the ocular method.

(b) Efficiency of optical system

At this point it becomes necessary to define a condition which will be referred to quite often in the following discussions. The optical system comprising any given polariscope must be so utilized that the highest possible sensitivity is attained in getting the zero. All the polariscopes reviewed, therefore, will be analyzed to see if they are being operated at the "maximum possible efficiency of the optical system."

The ocular polariscopes translate changes in light intensity, dI , directly into degrees of rotation, $d\theta$. Operation at maximum sensitivity would require that $dI/d\theta$ be a maximum at the zero of the instrument.

In the case of the total extinction instrument, $dI/d\theta$ should be a maximum at $\theta = \pi/2, 3\pi/2$, etc. Actually the case is as follows:

$$(1) \quad I = I_0 \cos^2 \theta,$$

$$(5) \quad dI/d\theta = -2I_0 \cos \theta \sin \theta.$$

At $\theta = 0, \pi/2, \pi$, etc., $dI/d\theta = 0$. At these points the instrument is least sensitive. Thus the total extinction instrument, using the eye as the observer of intensity, is actually operating at lowest efficiency.

At the most sensitive position of the two nicols, the absolute value of $dI/d\theta$ will be a maximum.

$$(6) \quad d^2I/d\theta^2 = -2I_0 \{ \cos^2\theta - \sin^2\theta \} = 0,$$

$$(7) \quad \cos^2\theta = \sin^2\theta,$$

$$(8) \quad \cos^2\theta = 1 - \cos^2\theta,$$

$$(9) \quad \theta = \cos^{-1} \sqrt{2}/2 = (2n - 1) \pi/4.$$

For values of θ given in equation (9), $dI/d\theta$ is either a maximum or a minimum. Inasmuch as the absolute value of $dI/d\theta$ is the same at both the maximum and minimum, the total extinction instrument is operating at highest efficiency when $\theta = 45^\circ, 135^\circ$, etc.

When the double field ocular polarimeter is used, the greatest theoretical sensitivity should be obtained when $\Delta = 90^\circ$. This value can be deduced from the above considerations.¹ Actually, Δ varies from 3° to 15° because the field intensity must be kept low, as explained in the preceding section. Here again, the use of the eye causes the optical set-up to be used at low efficiency.

(c) D.C. photoelectric methods

One type of photoelectric polarimeter parallels closely the total extinction polariscope shown in Fig. 12.² In keeping

¹See Appendix for mathematical proof.

²D. R. Morey, R. S. I., 3, 24 (1932). Schonrock and Einsporn, Physik. Zeitschrift, 37, 1 (1936).

with the considerations of the above paragraphs and the conclusion in equation (9), the zero is found by interpolation of the readings of the photoelectric current taken when $\theta = 45^\circ$ and $\theta = -45^\circ$. An arrangement is made to remove the error due to the absorption of light by the optically active medium. Accuracy up to 0.01° is claimed by this method. To achieve this, however, a very constant light source and a very steady amplifier are necessary. A rotation of 0.01° is equivalent to the detection of a change in intensity, dI , of $1.7 \times 10^{-4} I_0$.

$$dI = -2I_0 \cos \theta \sin \theta d\theta;$$

therefore

$$(5) \quad dI = -2I_0 \cdot \frac{1}{2} \cdot 1.7 \times 10^{-4} = -1.7 \times 10^{-4} I_0$$

$$(1.7 \times 10^{-4} \text{ radians} = 0.01^\circ).$$

This would require that the light source and amplifier be steady to the order of 0.02% which is well nigh impossible with present methods.

To eliminate the variations in the light intensity as a source of error, a system using split beams was designed.¹ The

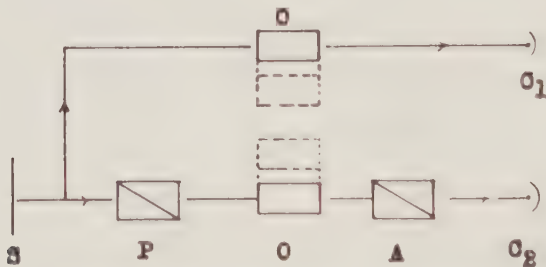


PHOTO-ELECTRIC POLARISCOPE

Fig. 16

¹Ebert and Kortum, Zeitschrift fur physik. Chem., (B) 13, 111 (1931).

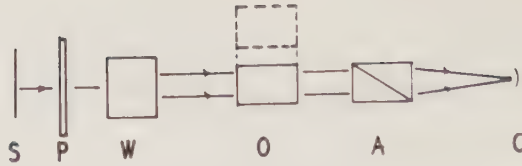
general set up of the optical path is shown in Fig. 16. The beam is split in two; one then passes through the polarizer, optically active medium, and the analyzer, while the other unpolarized beam passes to a tube containing the same optically active medium. The analyzer and polarizer are held at $\theta = 45^\circ$ in order to obtain maximum sensitivity. The two light beams terminate in two photocells, C_1 and C_2 , whose currents are either amplified by suitable D.C. amplification or detected by electrometers. By arranging the electric circuits so that the currents from the two photocells oppose each other, the instrument can be used with a null method of detecting the zero. The objection to such a method is that the assumption is made that the two photocells have the same characteristics and respond exactly alike to the same light flux changes. This again is a difficult matter to arrange and puts a definite limit on the attainable sensitivity.

No attempt has been made to review here all the methods of D.C. application of photocells to polarimetry. It is clear, however, that the instability of the light source and the amplifier limit the attainable accuracy of such instruments.

A. C. Photoelectric Methods

Recently, there has been developed independently here and in other laboratories¹ a method of detecting rotation which is independent of random variations of intensity of the light source and yet depends on only one photocell for observation. Essentially, the optical path, save for minor differences in the various models, is as follows:

¹Schonrock and Einsporn, Physik. Z., 37, 1 (1936). Kent and Lawson, Journal Opt. Soc. America, 27, 117 (1937).



A. C. Polariscopes

Fig. 17

The light from the light source, S, passes through a polarizer, P, which rotates at a constant speed. This light then is split into two plane polarized beams, the planes of polarization of which, differ by 90° . A Wollaston prism can be used to accomplish this. As in the case of the other polariscopes, the analyzer can be rotated and its angular position read on a graduated turn table.

Let α = angle between the plane of polarization of the polarizer and the upper field of the Wollaston prism, W, at a given instant of time, t.

Then $\frac{\pi}{2} - \alpha$ = corresponding angle with lower field at same instant t.

Let θ = angle between the plane of polarization of upper field of W and the plane of the analyzer, A.

Then $\frac{\pi}{2} - \theta$ = corresponding angle with lower field of W.

The intensity of light coming through the upper half of the optical path at time t is:

$$(10) \quad I_1 = I_0 \cos^2 \alpha \cos^2 \theta .$$

Similarly, the intensity coming through the lower path at same time t is:

$$(11) \quad I_2 = I_0 \cos^2 \left(\frac{\pi}{2} - \alpha \right) \cos^2 \left(\frac{\pi}{2} - \theta \right) = I_0 \sin^2 \alpha \sin^2 \theta .$$

If both beams are then focused on the same spot of the photocell

cathode surface, the total current, I_f , is the sum of the individual currents in both halves.

$$(12) \quad (I_f)_t = F_0 \cos^2 \alpha \cos^2 \theta + F_0 \sin^2 \alpha \sin^2 \theta,$$

where $F_0 = f(I_0, a)$, a = area of cathode surface exposed. Since α is a function of t , the current generated by the photocell will be A.C. There is, however, one value of θ for which the photocell current is constant irrespective of the value of α .

The rate of change of I_f with α (the A.C. generated by the photocell) is:

$$(13) \quad \frac{dI_f}{d\alpha} = F_0 [-2 \cos \alpha \sin \alpha \cos^2 \theta + 2 \cos \alpha \sin \alpha \sin^2 \theta] \\ = 2F_0 \cos \alpha \sin \alpha [\sin^2 \theta - \cos^2 \theta].$$

Setting $dI_f/d\alpha = 0$, we get

$$(14) \quad 2F_0 \cos \alpha \sin \alpha [\sin^2 \theta - \cos^2 \theta] = 0, \\ \sin^2 \theta = \cos^2 \theta,$$

$$(15) \quad \theta = \pi/4 = 45^\circ, \\ \frac{\pi}{2} - \theta = \pi/4 = 45^\circ.$$

Thus when the plane of polarization of the analyzer is exactly between the planes of polarization of the two fields of W , there is no A.C. generated by the photocell. This is the zero of the instrument and is detected by the use of earphones or rectifying devices. When this method has been applied, the results have been fairly satisfactory, sensitivity up to 0.02° having been obtained. The sensitivity is limited by the noise characteristics of the amplifier used to amplify the photocell current.

A careful study of the properties of such a circuit will show, however, that the prevailing methods for detecting the zero

have not utilized completely the possibilities of the instrument. Theoretically it should be possible to attain much greater accuracy.

The diagram in Fig. 17 shows the independent optical variables which determine the properties of the circuit. By fixing one of the variables, either α or θ , the effect of the variation of the other on the light intensity reaching the photo-cell can be studied.¹

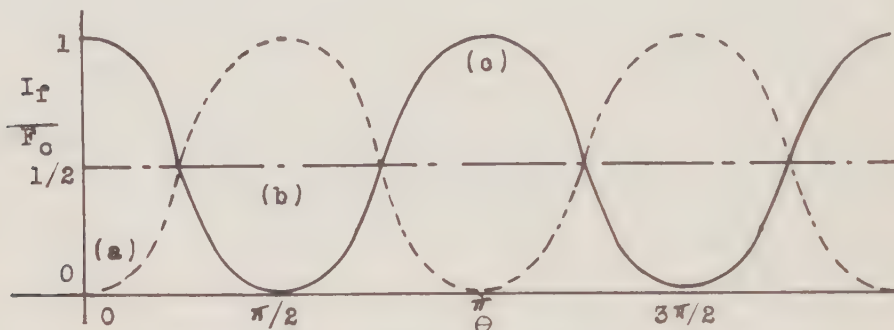


Fig. 18

Based on equation (12), Fig. 18 shows I_f/F_0 as a function of α for three different fixed positions of θ .

(a) When $\theta = \pi/2$, equation (12) becomes:

$$I_f/F_0 = \sin^2 \alpha .$$

This curve has maxima at $\alpha = (2n - 1)\pi/2$ and minima at $\alpha = 2n\pi/2, 0$, where n is any integer.

(b) When $\theta = \pi/4$, equation (12) becomes:

$$I_f/F_0 = 1/2.$$

Here, the variation of α has no effect on the value of I_f/F_0 . This, of course, was shown in equation (15).

¹See Appendix for more extended discussion of material.

(c) When $\theta = 0$, equation (12) becomes:

$$I_f/F_0 = \cos^2 \alpha .$$

This curve is very similar to that of (a) except that the maxima and minima are interchanged.

Translated into experimental terms, the curves in Fig. 18 represent what is seen in an oscillograph which is connected to the output of the amplifier of the photocell current. As the value of θ is varied from $\pi/2$ to 0, the curves change in structure from those of (a) through (b) to (c).

Let us examine this family of curves at the point $\alpha = \pi/2$. For $\theta = \pi/4$, the amplitude, X , of the alternating current generated by the photocell is zero. For $\theta = \pi/2$, the amplitude is $\frac{I_f/F_0}{2}$ and for $\theta = 0$, $X = \frac{-I_f/F_0}{2}$. It can also readily be seen that there is a phase change of 180° when θ crosses the value of $\pi/4$ (i.e., the amplitude changes sign).

By making a suitable transformation of equation (12) it is possible to plot X as a function of θ .

$$(12) \quad I_f = F_0 \cos^2 \alpha \cos^2 \theta + F_0 \sin^2 \alpha \sin^2 \theta .$$

Let $\theta = \frac{\pi}{4} + \delta$. This amounts to moving the zero of the graph in Fig. 18 from $\theta = 0$ to $\theta = \pi/4$.

$$(16) \quad I_f = F_0 [\cos^2 \alpha \cos^2 (\frac{\pi}{4} + \delta) + \sin^2 \alpha \sin^2 (\frac{\pi}{4} + \delta)] .$$

At $\alpha = \pi/2$:

$$(17) \quad \begin{aligned} I_f &= F_0 [\sin^2 (\frac{\pi}{4} + \delta)] \\ &= F_0 [\sin^2 \frac{\pi}{4} \cos^2 \delta + \cos^2 \frac{\pi}{4} \sin^2 \delta + \sin \frac{\pi}{4} \cos \frac{\pi}{4} \sin \delta \cos \delta] \end{aligned}$$

(note: $\sin (\frac{\pi}{4} + \delta) = \sin \frac{\pi}{4} \cos \delta + \cos \frac{\pi}{4} \sin \delta$),

$$(18) \quad I_f = F_0 [\frac{1}{2} + \cos \delta \sin \delta] ,$$

$$(19) \quad \frac{I_f}{F_0} - \frac{1}{2} = X = \sin \delta \cos \delta .$$

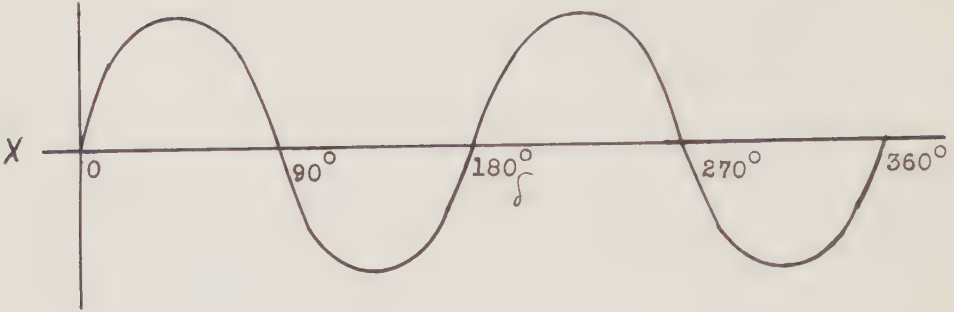


Fig. 19

With the aid of equation (19) and Fig. 19 we are now in a position to analyze the A.C. polariscope and determine under what conditions maximum efficiency of the optical set-up is obtained. Let us consider the case where earphones are used to detect the zero. If the polarizer is rotating at a fixed frequency, f , the earphones will give a tone of frequency $2f$, when $X \neq 0$. At the point where $X = 0$, there will be no tone of frequency $2f$ from the earphones. The intensity of the sound heard in the earphones is a function of the square of the amplitude of the A.C. generating the sound. Therefore

$$(20) \quad S = kX^2 = \cos^2 \delta \sin^2 \delta ,$$

k is a proportionality factor.

If we now plot S , the sound intensity, as a function of δ , we get the curve of Fig. 20. At the points $\delta = 0, 90^\circ, 180^\circ, 270^\circ$, etc., there is no sound. The analyzer turntable, therefore, shows a zero reading at those points. The accuracy with which the zero reading can be reproduced and the resulting sensitivity of the instrument are functions of $dS/d\delta$ at the zero. From equation (20),

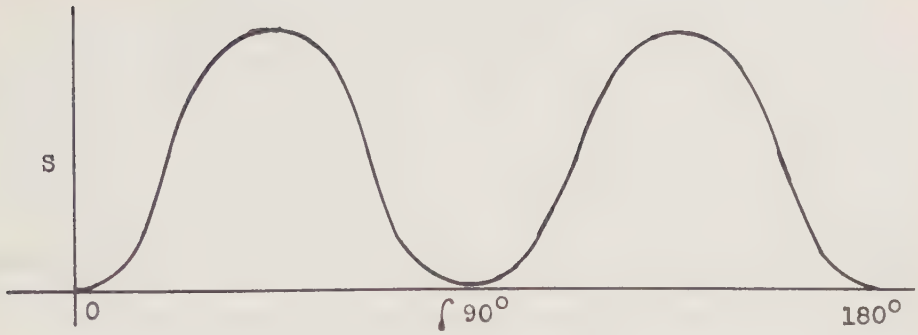


Fig. 20

$$\begin{aligned}
 (21) \quad \frac{dS}{d\delta} &= -2 \cos \delta \sin^3 \delta + 2 \sin \delta \cos^3 \delta \\
 &= 2 \sin \delta \cos \delta [\cos^2 \delta - \sin^2 \delta].
 \end{aligned}$$

At $\delta = 0$, $dS/d\delta = 0$. This means that the rate of increase of sound is smallest near the zero of the instrument. Therefore it can be concluded that the apparatus as described operates at lowest efficiency. Added to this is the fact that there is a threshold value of sound intensity below which the ear cannot detect a tone. We thus have here a situation very similar to the ocular total extinction polariscope described in the first chapter. This polariscope is, therefore, not much of an improvement over the polariscopes described before.

In a similar way, it can be shown that any other method of detecting the zero which depends on the rectification of the A.C. impulse, results in the kind of a signal which varies as a function of X^2 . The conclusion to be drawn from the above considerations is that while the existing A.C. methods have removed the errors involved in the fluctuations of the light source, the instruments so used are operating at minimum efficiency of the light circuit. It is difficult, therefore, to expect high sensitivity of the order of 0.001° from such methods.

A. C. Photoelectric Methods, Phase Shift Determination

It is possible to detect the zero by a method which depends linearly on X . As shown in Fig. 19, X varies from $\frac{+I_f/F_0}{2}$ to $\frac{-I_f/F_0}{2}$. As X passes through the value zero, the phase of the A.C. electric current changes by 180° , as shown in Fig. 18. We shall redefine the zero as the point where the sign of X changes. This point can be detected if the A.C. generated by the polariscope is related to another A.C. having the same frequency and having a constant phase value.

This principle was recognized implicitly in the design of the Hardy Spectrophotometer.¹ The current from the photometer supplies the field current of a small motor which rotates the analyzer prism, whereas the armature current is taken from an A.C. with the same frequency and a constant phase. When there is no A.C. from the photometer, the motor is stopped. When the analyzer A is off the zero, the motor will rotate in the direction determined by the phase relationship of the two currents. The energy moving the motor is a function of the product of the two currents; which amounts to multiplying amplitude, X , by a constant factor. Using such a set-up, a reproducibility of the zero within 0.05% is reported. Translated into terms of rotation of plane of polarization, it amounts to a sensitivity of about 0.02° . It is conceivable that the use of more sensitive detecting devices such as a dynamometer or a balanced modulator vacuum tube set-up should increase the accuracy of the method by at least ten fold.

A study of Fig. 19 and equation (19) will show that a method of detection of the zero, which depends linearly on the

¹A. C. Hardy, Journal Opt. Soc. of America, 25, 305 (1935).

value of X , has its maximum sensitivity at the zero. Using the same calculation as on page 28 it is shown that a detection of 0.001° requires sensitivity to a change in the value of X of 1.7×10^{-5} of the maximum value of X obtainable. Thus the same order of sensitivity is obtained by such a method as by total extinction or half-shadow polariscopes operating at maximum efficiency.

A polariscope, based on the above principles, has been built in this laboratory. Preliminary observations have shown that it follows all predictions made of the "phase shift method," and with the insensitive instruments at hand it has a sensitivity of $.02^\circ$. It is most sensitive about the zero, and the curve of the deflection of a galvanometer against the rotation of the analyzer is exactly like the curve in Fig. 19 (the deflection of the galvanometer is assumed proportional to X). It is hoped that the proper adjustment of the amplifier and the phase change detector will result in the ability to detect a rotation of 0.001° .

APPENDIX

To prove that the greatest theoretical sensitivity is obtained when $\Delta = 90^\circ$. From (2)

$$dI = I_0 \cos^2(\theta + \Delta) - I_0 \cos^2\theta$$

(dI refers to the difference in intensity of the two fields).

$$\frac{dI}{d\theta} = 2I_0 \cos \theta \sin \theta - 2I_0 \cos(\theta + \Delta) \sin(\theta + \Delta).$$

To obtain the maximum,

$$\frac{d(dI/d\theta)}{d\Delta} = 2I_0 \sin^2(\theta + \Delta) - 2I_0(\cos^2[\theta + \Delta]) = 0,$$

$$\cos^2(\theta + \Delta) = \sin^2(\theta + \Delta).$$

Taking the square root of both sides;

$$\cos(\theta + \Delta) = \sin(\theta + \Delta),$$

$$\cos \theta \cos \Delta - \sin \theta \sin \Delta = \sin \theta \cos \Delta + \cos \theta \sin \Delta,$$

$$\frac{\cos \Delta - \sin \Delta}{\cos \Delta + \sin \Delta} = \tan \theta.$$

From (3)

$$\frac{\cos \Delta - \sin \Delta}{\cos \Delta + \sin \Delta} = \frac{\cos \Delta - 1}{\sin \Delta}.$$

This leads, finally, to:

$$\sin \Delta = 1 - \cos \Delta.$$

There are two solutions to the last equation. One, when $\Delta = 0^\circ$, is ruled out because a single field instrument results. The other, when $\Delta = 90^\circ$, is, therefore, the setting of the two

polarizer prisms which gives the greatest change, $dI/d\theta$.

To study the properties of the family of curves in Fig. 18.

$$(16) \quad I_f/F_0 = \cos^2 \alpha \cos^2(\frac{\pi}{4} + \delta) + \sin^2 \alpha \sin^2(\frac{\pi}{4} + \delta),$$

$$\begin{aligned} \frac{d(I_f/F_0)}{d\alpha} &= -2 \cos \alpha \sin \alpha \cos^2(\frac{\pi}{4} + \delta) \\ &\quad + 2 \sin \alpha \cos \alpha \sin^2(\frac{\pi}{4} + \delta) \\ &= \sin 2\alpha [\sin^2(\frac{\pi}{4} + \delta) - \cos^2(\frac{\pi}{4} + \delta)]. \end{aligned}$$

When $\sin^2(\frac{\pi}{4} + \delta) - \cos^2(\frac{\pi}{4} + \delta) = 0$, the slope is zero regardless of the value of α . When, however, $\sin^2(\frac{\pi}{4} + \delta) - \cos^2(\frac{\pi}{4} + \delta) \neq 0$

$$\frac{d(I_f/F_0)}{d\alpha} = A' \sin 2\alpha,$$

where

$$A' = \sin^2(\frac{\pi}{4} + \delta) - \cos^2(\frac{\pi}{4} + \delta).$$

The zero values of this new curve are $\alpha = 0, \pi/2$, etc. These, in turn, determine the maxima and minima of the original curve.

Whether they are maxima or minima depends on the value of A' .

For

$$\frac{d^2(I_f/F_0)}{d\alpha^2} = 2A' \cos 2\alpha.$$

If A' is positive, the maxima are: $\pi/2, 3\pi/2$, etc.

If A' is negative, the maxima are: $0, \pi$, etc.

The value of A' is a function of δ .

$$\sin^2(\frac{\pi}{4} + \delta) - \cos^2(\frac{\pi}{4} + \delta) = A'.$$

If $0 < \delta < \pi/4$, $A' > 0$. If $\pi/4 < \delta < \pi/2$, $A' < 0$.

If $0 > \delta > -\pi/4$, $A' < 0$. If $-\pi/4 > \delta > -\pi/2$, $A' > 0$.

It will be noticed that when A' changes sign, there is a change in phase of π , for the maxima are replaced by minima and vice versa. The points of change of phase are $\delta = \pm n\pi/2$, where

$n = 0, 1, 2$, etc. The phase value is dependent only on the sign of A' ; not on its absolute value. The value of A' is directly proportional to X in equation (19).

